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27 April 2015

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Voïtchovsky, K. (2015) 'High-resolution AFM in liquid : what about the tip?', Nanotechnology., 26 (10). p. 100501.

Further information on publisher's website:

<http://dx.doi.org/10.1088/0957-4484/26/10/100501>

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High-resolution AFM in liquid: what about the tip?

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Abstract

Atomic Force Microscopy relies on a nanoscale tip to image and probe samples, often down to the sub-nanometre level. The measurement process depends on the precise geometry and chemical nature of the tip apex, and is therefore difficult to control. In the current issue of Nanotechnology, Akrami and co-workers show that, for measurements in aqueous solutions and on flat samples, the presence of stable hydration sites at the tip apex is key to achieving high-resolution images. These sites can be created on commercial tips using a simple preparation strategy that prevents build-up of interfering contaminants. The findings by Akrami *et al* also suggest a possible way forward to control the influence of the tip on high-resolution measurements.

Since its invention, atomic force microscopy[1] (AFM) has rapidly become a technique of choice for surface and interface science. The success of AFM is largely due to its ability to measure molecular forces, and to work in liquid where it can probe atomic-level details of interfaces.

The potential of AFM is enormous for nanoscale science and technology especially in systems where the ability to operate locally is important. Examples of applications span processes as disparate as heterogeneous catalysis[2], nanoscale friction[3] and lubrication[4], wetting[5], the mapping of ionic effects[6] and biomolecular function[7]. Recent developments have extended the technique's reach even further, enabling video-rate measurements[8], nanomechanical mapping of a samples' viscoelastic properties using multiharmonics[9], and achieved significant improvements in resolution, with atomic-level resolution becoming routine[10].

Despite all these advances, AFM still suffers from a basic but important issue that often precludes quantitative measurements: the structural and chemical details of the nanoscale tip used to conduct the measurement are, in most cases, not known. This is because a full characterisation of the tip is a challenging, time consuming task, and likely to be destructive for the tip. Furthermore, a successful characterisation would not necessarily correlate with subsequent measurements

due to possible contamination. As a result, most reports of AFM measurements do not appropriately discuss tip effects or simply ignore them altogether. In liquid, the problem is exacerbated by the fact that solvation forces play an important role. As a result, the tip can dramatically influence measurements depending on its chemical composition[11], the particular geometry of its apex[12], and its surface charge[6]. If the tip is sharp enough, measurements tend to be dominated by the solvation structure of the sample and the influence of the tip is minimal, at least for flat samples[13].

In all cases, however, reproducibility and reliability remain major challenges for high-resolution measurements, primarily due to tip contamination. Most AFM tips are produced commercially, shipped in gel boxes and used several weeks after manufacture. This is ample time for contamination, which occurs in a matter of minutes, typically due to organics from the package or the surroundings[14]. Organic contamination is almost invariably detrimental to high-resolution, especially in aqueous solvents where it renders the tip locally hydrophobic and the hydration of the tip apex unstable.

In the current issue of Nanotechnology, Akrami and co-workers[15] tackle this issue upfront with a systematic study of treatment methods for commercial AFM tips, always evaluating the outcome of the process with atomic-level imaging in water. This study is an important first step towards a better characterisation of the tip influence on AFM measurements in liquid.

The authors demonstrate that the key to high-resolution imaging on flat surfaces is the creation of stable local hydration sites at the tip apex. The role played by these sites is twofold; first they support stable hydration forces between the tip and the sample thus enhancing resolution and allowing reproducibility. Second, the sites prevent the adsorption of organic contaminants once immersed due to their strong affinity for water. Akrami *et al.* show that stable hydration sites can be obtained by Si-sputtering on commercial tips: the sputtered silicon oxidises once in ambient conditions, with wet oxidation proving the most effective.

Interestingly, despite being composed of silicon, the commercial tip used for the experiment could not provide reliable high-resolution images in water prior to its sputtering. This indicates an initial lack of stable hydration sites at the tip apex, which the authors attribute to the presence of an organic contamination layer remaining in place even after aqueous immersion. A detailed understanding of the differences between the contamination of commercial and freshly Si-sputtered tips is still lacking, and would be highly valuable given the quasi-ubiquity of commercial silicon tips in AFM measurements.

The authors also explore alternative tip treatments such as UV/O₃ cleaning, Ar plasma and Ar sputtering. All treatments improved the resolution but not as efficiently as Si sputtering due to a lack of stable hydration sites.

The strategy proposed by Akrami *et al.* offers a simple yet reliable way around the contamination problem: organic contamination occurs inevitably, but appropriate tip preparation ensures that it is spontaneously removed once immersed in water, at least if done relatively rapidly after the treatment.

The need for a stable hydration site is also an interesting result because it sets a rationale for future tip improvements, including the design of strategies allowing tip characterisations better suited for high-resolution imaging.

Tip treatments are however often detrimental to tip sharpness and the next steps, aside from a better understanding of fouling mechanisms at the molecular level, will be the development of suitable strategies for imaging non-ideal interfaces such as highly curved[16] and deformable samples where convolution effects are important and tip sharpness critical.

Beyond imaging, fully quantitative measurements at the nanoscale would require a way to reliably control the shape of the tip apex[17] and its hydration sites. This is no doubt a formidable challenge, but its success would unlock unprecedented possibilities for surface and interface science, and allow AFM to fulfil its true potential.

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